

# Observation of room-temperature spontaneous phase segregation in overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ single crystals

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The occurrence and development of phase inhomogeneity in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals have been investigated by measuring their superconducting transition patterns using a high-sensitivity ac magnetometer. We find that the overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals, even if they were single-phased immediately after a high-temperature annealing process, show progressively pronounced multiple superconducting transitions with time as they were kept at room temperature in a dry air atmosphere. The results reveal that the oxygen dopants in the crystal are still mobile at room temperature. These dopants tend to re-arrange and thus form different phases, at a characteristic time scale of one or two weeks or so. Moreover, the diamagnetization loops in the newly segregated phase are very weak, presumably due to the existence of additional inhomogeneity down to a nanometer scale. Our results also show that the optimally doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  crystals seem capable to remain in a single phase with time.

That the cuprates are of a single phase at a given temperature and a carrier concentration is an essential assumption in the widely-used phase diagrams,<sup>1,2</sup> based on which many experimental aspects in the normal and superconducting states have been correlated and discussed. However, it is often a primary difficulty to obtain single crystals with high structural perfection and doping uniformity, yet with large enough size suitable for many experiments. Besides the electronic phase separation,<sup>3,4</sup> chemical phases separation at mesoscopic or even larger scales, often related to the inhomogeneous distribution or domain formation of oxygen vacancies or dopants, has also been observed in many families of the cuprates,<sup>5,6</sup> for examples, in  $\text{La}_2\text{CuO}_{4+x}$ ,<sup>7,8,9,10</sup> in lightly Sr-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,<sup>11</sup> in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ,<sup>12</sup> and in underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  where vacancy ordering domains of different types form at the chain layers.<sup>13,14</sup> Phase inhomogeneity has also been observed in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  by low temperature scanning tunneling microscopic studies.<sup>15,16</sup> With all these observations, however, one still cannot rule out the possibility that the phase separation is an extrinsic effect, avoidable if the crystals are grown up and annealed properly. In this paper, through investigating the time evolution of the diamagnetization signal, we show that the oxygen dopants in originally single-phased overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals tend to redistribute spontaneously at room temperature, which eventually and unavoidably leads to the occurrence of phase separation and inhomogeneity in the titled compound.

The  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals used in this experiment were proven to be of high structural quality and stoichiometric purity with the resolution limits of our X-ray diffraction and energy dispersion X-ray studies. To further guarantee the uniformity of the crystal, only those tiny pieces of crystalline sheets (typically

$0.5 \text{ mm} \times 0.5 \text{ mm} \times 0.05 \text{ mm}$ ,  $\sim 10^{-2} \text{ mm}^3$  in volume) cleaved and cut from the center of larger uniform ones were used for investigation. Each crystal was carefully annealed to maintain a certain and uniform level of overdoping. Then, its susceptibility was measured in a weak ac magnetic field (0.3 to 60 G) using a high-sensitivity vibration-sample magnetometer specially designed for measuring sub-millimeter-sized specimens.<sup>17</sup> This magnetometer uses a double-synchronous detection technique, with a high-frequency ac magnetic field at 10 kHz (at which the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  crystal is fully penetrated in the normal state), and a low-frequency vibration of the sample at 4.4 Hz. It reaches a resolution of  $1 \times 10^{-8}$  emu in susceptibility (or  $3 \times 10^{-10}$  emu in magnetic moments) for a sample of volume  $1 \text{ mm}^3$  in a field of 30 G. With such a sensitivity we can resolve any minority superconducting phase whose total volume is as small as  $10^{-7} \text{ mm}^3$ , at the same time without suppressing the superconductivity. Our measurement on optimally doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  crystals reveals a single sharp transition (will be shown in Fig. 5), which proves the reliability of this home-made setup on the one hand and the high quality of the pristine crystals used in this experiment on the other hand.

Figure 1 shows the superconducting transitions of two overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals, samples #1 and #1', measured immediately after an annealing treatment in  $\text{O}_2$  atmosphere at 550 °C for 52 hours. Sample #1 is measured in the configuration of  $B \perp c$ , whereas sample #1' is a small piece cut from sample #1, in order to be mounted into the quartz-tube sample holder in the  $B \perp ab$  configuration. The 10% to 90% transition width for sample #1' is  $\sim 1 \text{ K}$  in a field of 0.6 G perpendicular to the  $ab$ -plane, which demonstrates that an overdoped crystal could be in a uniform single phase.

For the case of  $B \perp c$ , the diamagnetization signal at

low temperatures reflects the nature of intrinsic Josephson couplings along the  $c$ -direction.<sup>18</sup> To distinguish the transition regime from this Josephson coupling regime, we find it helpful to plot the data in a logarithmic scale (the inset of Fig. 1). In such a plot the temperature dependence of the susceptibility is very steep in the transition regime but relatively “flat” in the Josephson coupling regime. The crossover between the two regimes takes place at  $\sim 82.5$  K for sample #1.

Although the overdoped crystals show a single superconducting transition if measured immediately after an annealing treatment, multiple transitions at different levels are always seen after the crystals have been kept at room temperature for a period of time. In our experiment, nine overdoped crystals have been examined, seven of them eventually exhibited a multiple transition pattern, and two of them underwent significant broadening in transition width, after they have been stored for a certain period of time.

Figure 2 shows the time evolution of the transition pattern for sample #2. This crystal was annealed in  $O_2$  atmosphere at  $450^\circ\text{C}$  for 48 hours. It was afterwards kept at room temperature in a dry air environment as protected by silica gel, which is a common way of sample storage in most of the laboratories. In a three-month period the susceptibility of the crystal in the  $B \perp c$  configuration was measured for several times. From the panel (b) of Fig. 2 it can be seen that the 88 K phase grew up significantly with time, and reached  $\sim 10\%$  in diamagnetization at the end of the three-month period.

The measurement performed in the  $B \perp ab$  configuration on sample #2' (which is a small piece taken from sample #2 at the end of the three-month period) also revealed the formation of a very pronounced secondary phase, as shown in the panel (a) of Fig. 2.

The growing up in volume of a higher- $T_c$  phase should reflect the change in local oxygen content and/or arrangement in the crystals. Only with such a mechanism can then the change be reversible, i.e., a single sharp transition can be restored by high-temperature annealing — which was exactly the case for our crystals. Our results therefore reveal that the balanced oxygen content in overdoped  $Bi_2Sr_2CaCu_2O_{8+x}$  is a function of the temperature and the oxygen partial pressure of the crystal's environment. The nearly balanced oxygen content in a crystal, as maintained by high-temperature annealing in  $O_2$ -atmosphere, must become over saturated as the crystal is cooled down to room temperature. Therefore, the oxygen dopants tend to redistribute and even to escape from the crystal, which finally creates the higher- $T_c$  phase. For this reason, the newly formed phase is likely near the edge of the crystals. It should occupy a substantially large volume, in order to cause an apparent diamagnetic signal of  $\sim 10\%$  for sample #2, and up to  $\sim 50\%$  for sample #2'.

The distinct multiple-transition pattern indicates the formation of two types of domains in the  $ab$ -plane of the crystal, each having a different oxygen content. The

mechanism of forming such domains might be similar to that of the vacancy ordering domains in underdoped  $YBa_2Cu_3O_{7-\delta}$ .<sup>13,14</sup> It has been shown through numerical simulations<sup>19</sup> that an ordered distribution of oxygen vacancies commensurate with the lattice, i.e., forming some types of staging, is energetically more favored than a random distribution.

A non-trivial mobility for the oxygen dopants at room temperature is another key factor for the occurrence of spontaneous phase separation. It has been shown in  $La_2CuO_{4+x}$  that the oxygen mobility is linked to the lattice imperfections, e.g., it is strongly enhanced by the presence of planar defects.<sup>20</sup> For  $Bi_2Sr_2CaCu_2O_{8+x}$  samples, the existence of incommensurate modulation along the  $b$ -axis<sup>21,22</sup> might in some way influence the oxygen mobility, which needs to be further studied.

Figure 3 shows the field dependence of the transition pattern of sample #2' three months after the annealing, and sample #2 24 days after the annealing. Two transitions can be recognized in weak magnetic fields, one onsets at  $\sim 81.6$  K and the other above 86 K. The nucleating and growing up of the superconducting domains below 86 K build up substantially large or enormous amount of diamagnetization loops in the  $ab$ -plane of the crystal. However, these loops are very weak, as they can be drastically suppressed by a field of  $\sim 1$  Gauss, and almost washed out by a field of a few tens Gauss. Such a sensitive field dependence should come from a Josephson-like weak superconductivity, reflecting the existence of additional inhomogeneity in the  $ab$ -plane of the newly segregated phase down to the coherence length scale.<sup>23</sup>

The diffusion process of the dopants to a lower-energy distribution is presumably driven by the thermal energy which is significantly lower at room temperature compared to that in high temperature annealing. This factor makes the diffusion process hardly completed, given rise to the additional inhomogeneity in the  $ab$ -plane. This picture seems consistent with the recent observation of energy gap inhomogeneity at nanometer scale using scanning tunneling microscopy.<sup>15,16</sup> With the best single crystals they obtained, Pan and co-workers found that the superconducting energy gap of  $Bi_2Sr_2CaCu_2O_{8+x}$  compound is inhomogeneous from place to place down to the nanometer scale, though the lattice is highly perfect.

Finally, Fig. 5 shows the transition patterns of two optimally doped  $Bi_2Sr_2CaCu_2O_{8+x}$  crystals (the 88 K phase) 15 days (sample #3) and six months (sample #4) after being annealed in Ar atmosphere ( $600^\circ\text{C}$ , two weeks). These crystals are from the same batch as sample #1 and #2. It seems that the tendency of spontaneous phase separation at room temperature is much insignificant for optimally doped crystals, as their transition pattern remains nearly the same after the six months period, and shows no significant field dependence at a level of a few Gauss. It indicates that the oxygen dopants in optimally doped crystals are near to a minimum energy distribution which is homogeneous down to the coherence length scale.

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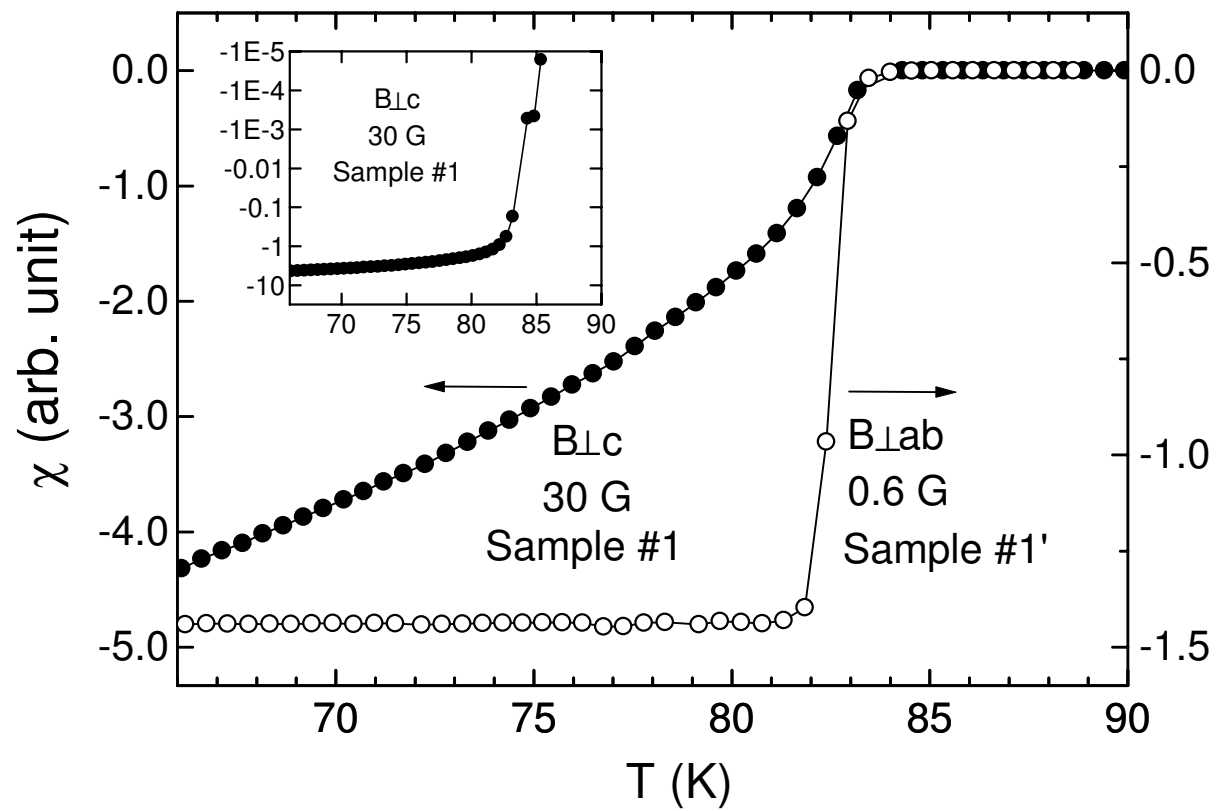
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  - <sup>23</sup> The sensitive field dependence of the transition pattern at a level of a few Gauss above 81.6 K is irrelevant to the irreversibility field  $H_{irr}$  nor to the upper critical field  $H_{c2}$ , because these fields are at a much higher level. Nor should the phenomenon be mainly caused by the amplitude fluctuation of the order parameter, otherwise we could hardly explain why the whole transition of the higher- $T_c$  phase depends sensitively on the applied field. Also, the magnetization of the higher- $T_c$  phase deduced from our susceptibility data does not follow the scaling law as expected for critical fluctuation (see Z. Tesanovic *et al.*, *Phys. Rev. Lett.* **69**, 3563 (1992); Q. Li, K. Shibutani, M. Suenage, *et al.*, *Phys. Rev. B* **48**, 9877 (1993)).

FIG. 1: The superconducting transition pattern of overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals measured immediately after an annealing treatment in  $\text{O}_2$  atmosphere at  $550^\circ\text{C}$ , showing a single and sharp transition. The inset is a semi-logarithmic plot of the data in the  $\text{B}\perp\text{c}$  configuration, which helps to distinguish the existence of any secondary superconducting phase in this configuration. Sample #1' is a small piece cut from sample #1.

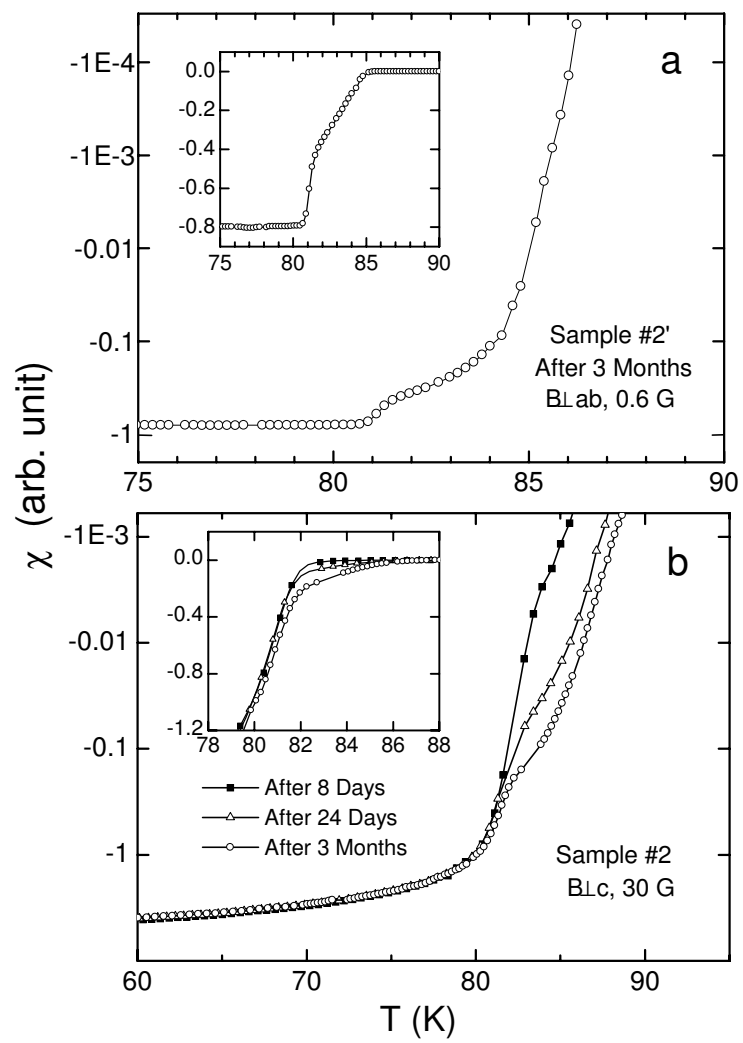
FIG. 2: The time-evolution transition patterns of overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals. A higher  $T_c$  phase gradually grows up as the crystals are kept at room temperature in a dry-air atmosphere. At the end of the three-month period, the newly segregated phase caused an apparent diamagnetization volume of  $\sim 10\%$  for the case of  $\text{B}\perp\text{c}$  (panel (b)), and up to  $\sim 50\%$  for  $\text{B}\perp\text{ab}$  (panel (a)) at 82 K.

FIG. 3: The field dependence of the multiple transitions of overdoped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  single crystals. Panels (a) and (b) are the susceptibility in the  $\text{B}\perp\text{ab}$  and  $\text{B}\perp\text{c}$  configurations, respectively. Panels (c) and (d) are the semi-logarithmic plots of the data in panels (a) and (b). Panels (e) and (f) displays the details of the onset-transition regions.

FIG. 4: The transition patterns of two optimally doped crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  15 days (sample #3) and six months (sample #4) after being annealed in Ar atmosphere at  $600^\circ\text{C}$ . Their transition patterns remain nearly the same, and shows no significant field dependence at a level of a few Gauss.



Wu, et al., Fig. 1



Wu, et al., Fig. 2

